Preparing chlorates

Chapter 1: Introduction

On an industrial scale, chlorates are prepared by electrolysis. Electrolyzing a solution of a chloride at elevated temperatures yields a chlorate. This method can be downscaled quite easily for amateur Pyro purposes. Other methods of chlorate manufacture exist that may be of interest for small scale use. They are usually less efficient but the economy of the process is not as important for amateur Pyro purposes as it is for industrial setups. A second method for example consists of heating a solution of hypochlorite. Sodium and calcium hypochlorite are both quite easily available as bleach and pool chlorinating agent respectively. Upon heating, the hypochlorite will decompose into both chloride and chlorate. The chlorate is separated and purified. Although slow and laborious, the method is simple and requires very little equipment. In the past chlorates were produced even on an industrial scale by bubbling chlorine gas through a hot hydroxide solution. This process is not very well suited for amateurs since chlorine gas is very dangerous to handle. The process is also extremely inefficient, for which reason it was abandoned quite soon after the electrochemical method became feasible at industrial scale.

Chapter 2: Electrolytic preparation

The electrolysis is carried out in a diaphragm-less cell, containing a solution of a chloride. Several chlorides may be used, but the use of sodium chloride has many advantages. Sodium chlorate is easily converted to a number of other chlorates by metathesis reactions. The most commonly used chlorates in pyrotechnics, potassium and barium chlorate, can both be made in this manner. Potassium chloride and barium chloride may also be used to obtain the respective chlorates directly, but this has many disadvantages as will be discussed below. Only sodium chlorate can be used in the manufacture of perchlorates, due to its high solubility.

Ammonium chloride should never be used, and should in fact not even be present in the cells in trace amounts. It could result in the formation of two dangerously sensitive and explosive compounds, nitrogen trichloride (NCl_3) and ammonium chlorate (NH_4ClO_3). The formation of both of these compounds should be avoided at all times. Not only can they explode by themselves when present in significant quantities, they can also lead to spontaneous ignition of pyrotechnic mixtures contaminated with even small amounts.

2.1 theory

Mechanism of chlorate formation

The reactions taking place in chlorate cells are not fully understood even today. A summarized description of the process will be given here, and the interested reader is referred to the literature listed below for a more extensive description.

The theory of Foerster and Mueller regarding the reactions in chlorate cells, developed about 80 years ago, is the most accepted. The following reactions are said to take place at the electrodes:

At the anode:

$$2Cl^- \longrightarrow Cl_{2(aq)} + 2 \text{ electrons}$$

At the cathode:

$$2H_2O + 2 \text{ electrons} \longrightarrow H_2 + 2OH^-$$

The dissolved chlorine gas can then react with water to give hypochlorous acid(HClO):

$$Cl_{2(aq)} + H_2O \longrightarrow HClO + H^+ + Cl^-$$

From this reaction it can be seen that if the chlorine does not dissolve but escapes to the atmosphere, no H^+ will be generated to neutralize the OH^- formed at the cathode and the pH of the electrolyte will increase.

The hypochlorous acid thus formed will react in acid-base equilibrium reactions with water to give hypochlorite ions and chlorine gas (dissolved). The exact concentrations of dissolved Cl_2, Hypochlorite (ClO^-)and HClO depend on the pH, temperature and pressure among other things. In the solution, chlorate will be formed (mainly) by the following reactions:

$$2HClO + ClO^- \longrightarrow ClO_3^- + H^+ + 2Cl^-$$

and

$$2HClO + ClO^- + 2OH^- \longrightarrow ClO_3^- + 2Cl^- + H_2O$$

These reactions take place at a rather slow rate. Since this reaction pathway is the most efficient one as we will shortly come to see, the conditions in the cell are usually optimized to increase their reaction rate. The pH is kept within a range where HClO and ClO^- are simultaneously at their maximum concentration (which is at around pH=6). The temperature is kept between 60 and 80 degrees centigrade, which is a good compromise between the temperatures required for a high reaction rate, low anode and cell body corrosion and high chlorine solubility (remember the chlorine evolved at the anode has to dissolve in the solution to start with). Many cells also have a large storage tank for electrolyte in which the electrolyte is kept for a while to give these reactions some time to take place.

Alternatively, chlorate may also be formed by oxidation of hypochlorite at the anode as follows:

$$6HClO + 3\ H_2O \longrightarrow {}^3/_2\ O_2 + 4Cl^- + 2ClO_3^- + 12H^+ + 6 \text{ electrons}$$

Oxygen is evolved in this reaction, which means a loss of current efficiency (the energy used for oxidizing the oxygen in water to the free element is lost when the oxygen escapes to the atmosphere). When the reaction routes are worked out, it turns out that following this path 9 faradays of charge are required to produce 1 mole of chlorate,

whereas only 6 faradays are required to do that following the route mentioned earlier. Therefore, optimizing the conditions for that route improves current efficiency.

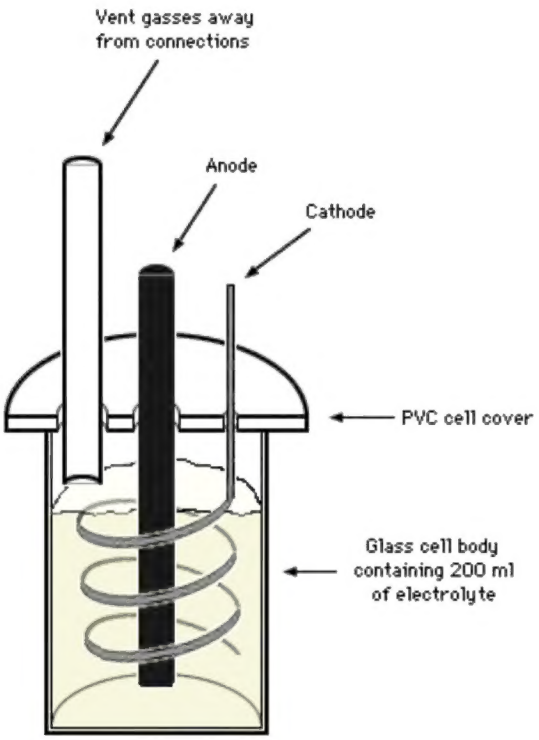
To prevent the products from being reduced at the cathode again, a membrane around the cathode was employed in the past. Today, small amounts of chromate's or dichromate's are added. A layer of hydrated oxides of chromium will then form around the cathode effectively preventing hypochlorite and chlorate ions from reaching the cathode surface.

Finally, it should be mentioned that the reactions forming perchlorates do not take place until the chloride concentration has dropped to below about 10%. Therefore, cells can be constructed and operated in such a way that chlorate is produced almost exclusively. The chlorate can then be purified and fed into a perchlorate cell. Depending on the type of anodes used in the chlorate cell, the purification step may also be skipped and the electrolysis continued until all chloride has been converted into perchlorate. Although slightly less efficient (and therefore not used a lot in industrial setups), this is much less laborious and therefore probably the preferred method for home setups.

Cell voltage

The current through a cell is related to the reaction rate. Therefore, to obtain a constant reaction rate that suits the cell design, a constant current is usually employed. The voltage over the cell will then fluctuate depending on conditions and cell design. The power consumed by the cell is the product of current and voltage, according to equation P = I * V. From that it can be seen that reducing the voltage over the cell results in a lower power consumption, an important fact for industrial operations. The factors influencing the cell voltage have been thoroughly investigated. Most important are the anode - cathode spacing, the concentration of the electrolyte, the surface area and materials of the electrodes, the temperature and the pH. Without going into details, the cell voltage usually lies in the range 3.5 - 4.5 volts. Of this, approximately 3 volts are required to get the oxidation of chloride to chlorate to take place (and the hydrogen reduction at the cathode), while the rest is used to overcome the resistance of the cell, according to Ohm's law V=I*R. From this law it can be seen that there are two ways to maintain a constant current through a cell: either the voltage over it may be varied or its resistance may be changed. Adjusting the voltage over a cell to maintain a constant current can be done manually or with an electronic circuit. If the power supply does not allow voltage adjustment (such as old PC power supplies or battery chargers for example) or the required electronics are not available, adjusting the resistance of the cell is another option. This could in principle be done by adjusting each of the factors mentioned earlier, the most practical of which is probably the anode-cathode distance. By increasing the distance between the electrodes the resistance of the cell is increased, which reduces the current through the cell. One thing to keep in mind when doing this is that it with decreasing resistance, the heat generated in the cell is increased. Depending on the anode material used it may then be necessary to cool the cell to prevent excessive erosion, more on that later.

2.2 Cell construction



Cells can range in complexity from a glass jar with a nail and a old battery electrode to well designed, corrosion resistant cells with thermostats, pH control, circulating electrolyte etc. Even the simplest of cells will work, but it will require more maintenance. If the chlorates are going to be prepared on a more or less regular basis, it probably pays to spend some more time designing a cell. It will also improve efficiency somewhat, but unlike in industrial setups where high efficiency is mandatory to be able to compete, the home experimenter can do with less efficient cells. The two main disadvantages of a low efficiency is that it takes more time for the conversion to complete, and that more electricity is required. To give some indication of the power consumption of the process: typical figures for industrial cells lie in the range 4.5 to 5.5 kWh per kg of sodium chlorate.

In this section some of the things to consider when building and designing chlorate cells will be discussed. The reader can design his own cell based on the information given. An example of a cell, the small test cell I currently use to experiment with, has been given but it is by no means perfect, and it is probably better to design your own. The example has merely been given to illustrate some principles.

2.3 An example

The example given here consists of a small cell, of 200 ml electrolyte volume. The cell is normally operated with graphite or graphite substrate lead dioxide anodes. Platinum sheet has also been tried with, unsurprisingly, good success. The electrolyte consists of sodium chloride with either some potassium dichromate or potassium fluoride added, depending on whether graphite or lead dioxide anodes are used. The cathode consists of a stainless steel wire spiraling down. The wire is corroded where it is not submerged, so it has to be replaced occasionally. The connections to the anode and cathode are made outside the cell but do corrode from the gasses and electrolyte mist. This is partially prevented by leading the gasses away from the connections with a vent tube, as shown in the picture. Covering the connections with hot melt glue also helps, but the heat generated in a faulty connection may cause the glue to melt.. The temperature is controlled by placing the cell in a water bath, which acts as a heat sink. If the temperature is too low, Styrofoam isolation is provided. The cell is operated outside, causing the temperature to fluctuate between day and night. The pH is checked about twice a day and adjusted if necessary with hydrochloric acid. The power source used is an old computer power supply. The output voltage can be regulated within certain limits and this is done to maintain a current of about 4 amperes. An other model computer power supply was used previously that did not allow control over the output voltage. Current adjustment was done by widening or narrowing the cathode spiral, effectively reducing or increasing the anode-cathode distance.

Theoretically, if 100% efficiency could be reached, the cell would have the capacity to convert approximately 35 grams of sodium chloride to 64 grams of sodium chlorate per day. Using a metathesis reaction with potassium chloride this would yield 74g of potassium chlorate. In practice the average yield is about 40 grams of potassium chlorate a day from which an efficiency of 55% can be calculated.

2.4 Cell volume

This is the main factor affecting a cells capacity, provided the power supply can provide the necessary current. As a rule of thumb no more than 2 amperes per 100 ml of electrolyte must be passed through a chlorate cell. Under more optimal conditions a higher amperage may be tolerable, still maintaining reasonable efficiency whereas in less optimal conditions 2 amperes may be too high and a lot of chlorine will be lost, leading to lower efficiency and rising pH. A current of 2 amperes will convert approximately 0.73 gram of sodium chloride to 1.32g of sodium chlorate per hour (assuming 100% efficiency). After extracting, metathesis reactions and recrystallizing that will yield 1.53 g potassium chlorate. So, for example, to produce 100 grams of potassium chlorate a day at least 100 grams / 1.53 grams / 24 hours * 100 ml = 272 ml of electrolyte is required. To maintain that rate of conversion the cell will then require 272 ml / 100 ml * 2 amperes = 5.44 amperes. If a cell is less efficient than 100%, which every cell is, increase these figures proportionally (so at 50% efficiency: 100% / 50 % * 272 ml = 544 ml of electrolyte, consuming 10.88 amperes of current to maintain the same rate of production). The example cell described above contains 200 ml of electrolyte. Thus, it should be operated at a current of 4 amperes, and the maximum daily yield is 100/272 * 200 = 74 g of potassium chlorate after processing the electrolyte. These figures were also mentioned in the cell description without explanation.

2.5 Cell body materials

One of the main problems in chlorate cells is the corrosiveness of the electrolyte. Only very few materials do not corrode when in contact with the electrolyte or its fumes. Most metals corrode, many plastics will and even glass does under some circumstances.

Some metals, such as steel, can be used if they are protected from corrosion in some way. For that purpose it can be coated with a resistant material such as Teflon or some types of rubber, or it can be **'cathodically protected'**. This means it is used as a cathode. The negative potential prevents the steel from being oxidized if the current density (current per unit of surface area) on the steel is high enough.

Some metals, such as titanium, zirconium, tantalum and niobium, form a protective film when they are in contact with the electrolyte. This prevents them from further corrosion, and they therefore find extensive use in industrial setups (particularly titanium because it is the cheapest). For amateurs the difficulties in working with these metals and their high price restricts their use somewhat. In small scale setups glass and plastics such as PVC are more easily available, easier to work with and much cheaper.

The table below gives some idea of how well a number of materials stand up to corrosion. The column 'protected' lists how well metals resist corrosion when cathodically protected. The column 'unprotected' lists materials used as is.

material	corrosion resistance when unprotected	corrosion resistance when cathodically protected
Iron	--	+
Stainless steel	-	+
Titanium	++	++
Copper	--	++
Brass	--	+
Tantalum	++	++
Platinum	++	++
Aluminum	--	+-
PET	++	X
Poly ethylene	+	X
Poly propylene	+	X
PVC	++	X
Rubber	+-	X
Hot melt glue	+-	X
Styrene	-	X
Graphite	+	+
Silicone rubber	--	X
Concrete	+	X
Glass	++	X
Ceramics	++	X
Wood	--	X
Polyester	-	X

2.6 Electrode materials

The range of suitable electrode materials is very limited. Especially the anode material is critical. The positive charge on the anode promotes oxidation and the evolving oxygen attacks many anode materials. Several anode materials have been considered over the years. Today's main options are listed below along with a short description.

Anode materials

Graphite: graphite is cheap and easy to obtain. It does however corrode at a comparatively fast rate. This makes it necessary to replace the anodes every so often and to filter the electrolyte before further processing which can be difficult and laborious due to the small size of the carbon particles. Graphite is not suitable for making perchlorates. When the chloride concentration of the electrolyte drops to the point where perchlorate formation begins (about 10% w/v), the graphite begins to oxidize at a great rate, yielding no or only traces of perchlorate. Cells operating with graphite anodes must also be maintained at a relative low temperature to limit anode erosion, which translates to a lower cell capacity. Graphite rods can be found in old manganese dioxide-zinc batteries or in welding shops where they are sold as 'gouging rods'. They can be treated with linseed oil to reduce corrosion. A practical method for the home experimenter has been devised by Rich Weaver, and is well described on Mike Brown's page. Old battery electrodes do not need to be treated with linseed oil.

Platinum: The obvious disadvantage of platinum is its high price. However, platinum anodes corrode only at a very slow rate and are suitable for perchlorate production. They therefore provide an almost ideal anode material. High efficiency can be reached with platinum and processing of the electrolyte is greatly simplified.

Lead dioxide: Lead dioxide provides an economical alternative to platinum. Lead dioxide anodes can be made at home. This takes some work and effort, but the anodes are cheap, fairly resistant to corrosion even at higher temperatures and are suitable for perchlorate production. More information on lead dioxide electrodes is given elsewhere on this homepage.

Manganese dioxide: Another oxide that is conductive and resistant to oxidation. It is made by thermal decomposition of manganese nitrate pasted onto a substrate. This type of anode seems quite promising for amateur Pyro use. For more information, the user is referenced to patents in the literature list below. If anyone has experiences with these anodes and their preparation I'd be most interested to hear about them.

DSA: DSA stands for Dimensionally Stable Anode. This is the common term used to refer to anodes consisting of a layer of noble metal oxides (usually RuO_2 and TiO_2) coated onto a substrate, usually titanium. This type of anode is finding increased use in industrial cells because of its comparatively low cost when compared to platinum and its resistance to corrosion. Some of the chemicals required to manufacture these anodes (particularly $RuCl_3$ and tetra-butyl titanate, $Ti(OBu)_4$) are expensive and perhaps difficult to handle safely. However, if the chemicals can be obtained and suitable equipment is available, the procedure to make the anode seems fairly straightforward and may be an option. For the preparation of these, the reader is referenced to the literature. Again, I'd be most interested in anyone's experiences with this type of anode.

Magnetite: This has found use in industry in the past, but is rarely used nowadays. It corrodes, but not very quickly and it can be used for perchlorate manufacture. The anodes are made by melting and casting $FeO.Fe_2O_3$ into the required anode shapes. I have little literature available on this material, so it is not further discussed here.

Cathode materials

Both stainless and mild steel find widespread use as cathode materials. Brass and copper may also be used. Each of these metals is protected to a certain extent by the negative charge present on the cathode as long as they are submerged and the current per surface area is high enough. Unsubmerged parts of the cathode corrode at a high rate however due to the action of evolving gasses and droplets of cell electrolyte.

It seems that under some conditions the chromium in stainless steel can dissolve, even though the cathode does not seem to corrode. A yellow electrolyte is the result from which barium chromate can be precipitated even if no chromate was added, which will be described later (see processing the electrolyte). The presence of chromates could lower the efficiency of cells employing lead dioxide anodes.

Finally, contamination of the final product with copper (from brass or copper erosion products) can be dangerous when the product is to be used in pyrotechnic purposes. Although this is unlikely to be a great problem since the impurities are usually removed easily and completely by filtration (as will be described later) it is good to be aware of the possibility.

2.7 pH and temperature control

Although not essential for chlorate manufacture, controlling the temperature and pH will increase cell efficiency and therefore the capacity of a cell. Temperature control can be anything from a sophisticated thermostat and heating element (or a cooling element) to simple insulation around the cell or a cold water bath. As mentioned earlier, part of the electric energy is lost as heat in the cell. Small cells operating at high currents can sometimes reach temperatures of 80 to 90 deg C. Though high temperatures will improve efficiency, temperatures as high as that will also increase anode corrosion and it is therefore usually considered better to maintain a temperature in the range 60 to 80 deg C to get the best of both worlds. Graphite anodes tend to erode faster than other types though, especially at higher temperatures, and cells employing these are therefore usually operated at 40 deg C to limit anode erosion.

Like temperature control, pH control is not essential for chlorate manufacture. Efficiency is improved greatly however if the pH is kept within the range 5.5 - 6.5 (slightly acidic) as explained in the theory section. Graphite anodes also tend to erode faster at high pH, so maintaining the pH will extend graphite anode life. In commercial setups pH control is done manually by periodic additions of hydrochloric acid. Automated pH control seems to be difficult and expensive to realize. If anyone devices a practical method of doing this, I'd be interested to hear about it.

2.8 Preparing the electrolyte

When just starting a first batch of chlorate a fresh electrolyte has to be prepared. When the cell has been operated before, the electrolyte from the previous cell is available to

prepare the electrolyte for a new batch. Also, the material left behind from the extraction and purification steps can be added to the next cell as it may contain some residual chlorate. That way no product left in the solution after processing is lost.

As mentioned, it is common to use sodium chloride to prepare sodium chlorate first, which is then converted to potassium or barium chlorate later. Even though both compounds may be prepared directly from potassium or barium chloride, using sodium chloride as a starting material has advantages. Mainly, it makes processing of the electrolyte much easier since sodium chlorate is very soluble. It is therefore easily separated from insoluble impurities which are almost always present. It will be assumed that sodium chloride is used. If for some reason the use of other compounds is desired, the procedure and amounts may need to be adjusted.

Preparing fresh electrolyte

1. Prepare a saturated solution of sodium chloride. Take about 40 grams for every 100 ml of solution and bring the solution to a boil. Then allow to cool to room temperature again. Some sodium chloride will crystallize as the solution cools. The solution is then filtered to obtain a clear saturated solution.

2. Optionally, 2 to 4 g/l of potassium dichromate, potassium chromate, sodium chromate or sodium dichromate may be added to improve efficiency. These compounds are suspected carcinogens, so if you choose to add any, know the hazards involved and act accordingly. If lead dioxide anodes are used, do not add potassium dichromate as it will only reduce efficiency. Instead, 2 to 4 g/l of sodium or potassium fluoride may be used. Although not carcinogenic, the fluorides are nasty compounds as well and should be handled properly.

3. Finally, the pH of the solution can be adjusted. A pH of around 6 is optimal, but anything between 5.5 and 6.5 is reasonable. The pH can be increased by addition of sodium hydroxide solution and it can be decreased by adding hydrochloric acid. Do not use too concentrated solutions for adjusting the pH. A concentration of 2% (w/v) for both solutions is convenient to work with.

Recycling old electrolyte

When electrolyte from a previous batch of chlorate is available the following steps can be used to recycle the electrolyte.

1. If the electrolyte is not clear but has solid particles in it, filter to remove these. See the section on filtering below.

2. dissolve any impure chlorate from the purification and extraction steps.

3. Now, re-saturate the solution with sodium chloride. The procedure mentioned above in step 1 of 'preparing a fresh electrolyte' may be used.

4. The chromate, dichromate or fluoride if added is still present so does not need to be replenished. The pH should be readjusted, like in step 3 for preparing a fresh solution above.

2.9 Operating the cell

Voltage and current 15Amps for 500 Sq cm of anode

As explained in the theory section the voltage over the cell may vary. The current should be kept more or less constant at a value determined by the cell design. As a rule of thumb, supply 2 amperes of current per 100 ml of electrolyte. If graphite anodes are used it is better to supply less current since that will increase anode life (30 mA per square centimeter of anode surface area is typical). A constant current supply is of course the most convenient to use for regulating current, but manually adjusting the voltage from time to time also works well. The current usually only changes very gradually, and the precise value is not very critical. In any case, measure the current at regular intervals and record them. That information is required to determine when a batch is complete, as described below in the paragraph 'running times'.

Maintaining optimal conditions

As explained, the pH of the electrolyte will tend to rise. Also, some of the water will evaporate and some will be consumed in the reaction. The temperature may also vary with ambient temperatures. For good efficiency these variables must be kept within certain limits.

Every once in a while, make up for evaporated and consumed water. This can be done with water, but it is better to use a saturated sodium or potassium chloride solution. That way, the chloride concentration will be kept at a higher level which improves efficiency. It will also prevent excessive formation of perchlorate, and in graphite anode based cells it reduces anode wear.

The pH will rise during operation of the cell, and it is best to lower the pH regularly to a value of about 6. A high pH value is best corrected by adding hydrochloric acid occasionally. If too much HCl is added, it may be corrected with sodium hydroxide solution. The pH is self correcting to a certain extend as well, since at very low pH the cell will produce more chlorine gas. This will then escape, raising the pH again. Measuring the pH of the solution can be done with common pH paper. However, if the paper is simply dipped directly into the electrolyte the hypochlorite present will usually bleach the paper making a measurement impossible. This problem can be overcome by boiling a sample of the solution for 5 minutes and measuring the pH of that. The boiling destroys the hypochlorite.

The temperature will usually reach a more or less constant value quickly. If the cell is placed outside, the temperature may vary between night and day and between seasons of course, so then some sort of control may be necessary to maintain the optimum. Usually,

cooling is necessary but it will depend on the specific cell design as explained in the theory section.

Running times Approx 7and a half days for my cell

The time required to convert a certain amount of chloride to chlorate depends on the current and the efficiency. The latter can vary dramatically from cell to cell and it is therefore not possible to state precise running times. It is however possible to calculate the required running times for a hypothetical cell operating with 100% current efficiency. The calculation will show that the conversion of one mole of chloride to chlorate requires 160.8 amperage hours. So, for example, a cell containing 100 grams of sodium chloride will require 100/58.6 * 160.8 = 274.4 Ah if it operates at 100% efficiency. For a current efficiency other than 100%, increase the running times in proportion (to convert 100g of NaCl with 80% current efficiency one needs 274.4/80*100 = 343 Ah). So, if a current of 3 amperes flows through the cell, it requires 274.4 / 3 = 91.47 hours (91 hours, 28 minutes) to finish.

2.10 Processing the electrolyte

When done, the product must be extracted from the electrolyte and the electrolyte can be recycled for the next batch (see preparing the electrolyte).

Filtering

The electrolyte usually contains suspended solid particles, even though they are not always visible. Suspended particles can be detected with the use of the Tyndall effect. Shine a bright flashlight through the side of a glass container containing the solution. If no suspended particles are present the light beam cannot be seen going through the solution. If suspended particles are present they will scatter the light and make the beam visible.

Usually, the impurities consist of erosion products of the anodes, the cell walls, and the unsubmerged parts of the cathodes. These particles may be very small and are not always easily removed with common filtering paper. Filtering through a layer of diatomeous earth (sold in shops for aquarium supplies) in a filter or on a piece of cloth sometimes solves the problem. Another great idea for a filter comes from E.S. However, just filtering will not always remove all solid impurities. A common impurity that is hard to remove is suspended iron hydroxide, originating from corrosion of (stainless) steel

cathodes. The fluffy, voluminous form of the material often gives it a white or yellowish foggy appearance. This is next to impossible to remove unless some sodium hydroxide or pool coagulant is added first. This causes the iron hydroxide particles to coagulate, making them easy to remove by filtration. Another possibility is to add hydrochloric acid to lower the pH to between 2 and 3. This will dissolve the iron hydroxide. If sodium hydroxide is then added to raise the pH to above 7 again, the iron hydroxide is precipitated in a more dense form which is easily removed by filtration, even with common filter paper.

In this step, the advantages of using sodium chloride will become evident. When potassium chloride is used instead potassium chlorate crystallizes during operation of the cell due to its relatively low solubility. To separate the potassium chlorate from insoluble impurities the electrolyte has to be filtered hot. The solution usually takes quite a long time to pass through the filter and if it cools during this time, potassium chlorate will crystallize and block the filter. Alternative methods have been developed to separate potassium chlorate from insoluble impurities. For example, the solution may be boiled and sufficient water added to dissolve all potassium chlorate. If the solution is then allowed to cool slowly, crystals of potassium chlorate will form on the suspended insoluble impurities. These will sink to the bottom, usually leaving a clear solution. The clear solution is then carefully decanted and allowed to cool further . This method will not remove the insoluble purities as well as filtering will but it is much less laborious.

Destruction of hypochlorite

Next, the electrolyte is boiled to decompose remaining hypochlorite. 15 minutes of vigorous boiling is sufficient. After that, the pH of the solution is checked and it is made slightly alkaline by adding sodium hydroxide solution. Bring the pH to between 8 and 9.

Metathesis reaction

At this point, a clear solution of sodium chlorate (with residual chloride) has been obtained. This can be used either to prepare potassium or barium chlorate (or other chlorates which are not further elaborated upon here), or it can be used to prepare perchlorates, described elsewhere.

Potassium chlorate is by far the most commonly used chlorate in pyrotechnics. For practical purposes, the preparation of this compound is discussed here. For the preparation of barium chlorate the amounts will have to be adjusted.

1. Weigh out either 127g of potassium chloride or 355g barium chloride for every 100 g of sodium chloride that was started with, depending on whether you want to prepare potassium or barium chlorate. Dissolve this in as little water as possible (dissolve in minimum amount of boiling hot water, add a bit more water and allow to cool. Nothing should precipitate. If it does, add some more water and heat again)

2. Add this solution to the electrolyte. A white precipitate of potassium or barium chlorate should form.

3. Bring the solution to a boil. Add 20 ml amounts of water to the solution in 5 minute intervals until all chlorate has dissolved. If all chlorate dissolves upon heating without the addition of extra water, allow the water to evaporate until a thin crust of chlorate forms on the surface (indicating that the saturation point has been reached). Then add 20 ml of water and boil for a minute to redissolve the crust.

4. Allow the solution to cool to room temperature. Potassium or barium chlorate will crystallize. If it has cooled to room temperature, cool further to 0 deg C.

5. Filter to obtain the crude chlorate crystals. Rinse them thoroughly with ice-cold water. The filtrate can be saved to prepare the next electrolyte, as is described in the section on recycling electrolyte.

2.11 Purifying the product

The crude product can be purified by recrystallization. The low solubility of potassium chlorate makes this method very convenient to use and will greatly improve the purity with a relatively small loss of product. Barium chlorate is somewhat more soluble and to prevent losses it is a good idea to use the impure barium chlorate 'waste' from this procedure in the electrolyte of a new cell. Some treatment is necessary, which was described earlier. If a single recrystallization step does not yield a sufficiently pure product, the method can be repeated to further increase the purity. Usually one or two recrystallizations will yield a product that does not impart the characteristic yellow color of sodium impurities to a flame.

1. Place the crude product in a pan and add 100 ml of water for every 35g of crude potassium chlorate or 50g of barium chlorate. Bring this to a boil.

2. Add 20 ml amounts of water to the boiling solution until all the chlorate has dissolved.

3. Check the pH of the boiling solution. It should be neutral or slightly alkaline. If it is acidic, add potassium hydroxide solution until it is slightly alkaline (pH 7..8) again. If this is not done, traces of acid may be included in the product making it very dangerous to use in pyrotechnic compositions.

4. Allow the solution to cool to room temperature. The chlorate will crystallize.

5. Filter and rinse the crystals in the filter well with ice cold water. The filtrate may be used to prepare the electrolyte for a new cell, as was described in the section on recycling old electrolyte.

6. The crystals may be dried in an oven at 100 deg C.

Thermal decomposition of hypochlorites

This is an alternative method of chlorate manufacture. It is more laborious than the electrolytic method, and can only be used for small batches at a time. The starting materials are quite easily available however as bleach and pool chlorinating agents and it only requires the use of simple tools.

3.1 Starting materials

Possible starting materials are sodium hypochlorite and calcium hypochlorite. The former is available in solution as bleach and antifungal spray for bathrooms. Calcium hypochlorite finds use as a chlorinating agent for pools. However, different varieties exist. Carefully read the package to make sure you have the right material. It usually states a '85% available chlorine' content for calcium hypochlorite. A higher available chlorine content may mean it is something else, most likely trichlorohydrocyanuric acid.

3.2 Method

Depending on the starting material, sodium or calcium hypochlorite, a different procedure must be followed. Each is described separately below.

Procedure when using sodium hypochlorite

It is assumed bleach will be used, which is usually a 4% solution of sodium hypochlorite in water. If a less or more concentrated solution is used, adjust the amounts accordingly.

1. Take 1 liter of bleach, and place this in heat resistant glass or stainless steel container. Bring it to a boil.

2. Boil the solution until only about 140 ml of solution is left. The exact volume is not critical, a deviation of 10 to 20 ml is acceptable.

3. Allow the solution to cool. If crystals form upon cooling, filter the solution after it has completely cooled. The crystals are sodium chloride and can be discarded.

4. In a separate container, prepare a solution of potassium chloride. Dissolve 28 grams of potassium chloride in the smallest volume of water possible (about 80 ml). This can be done by dissolving the potassium chloride in about 90 ml of boiling water, and allowing it to cool. If crystals form, add some more water, boil again to dissolve the potassium chloride, and allow to cool again. If crystals form, repeat. If not, the solution is ready to use.

5. Mix the boiled bleach solution with the potassium chloride solution. A white precipitate should form. This is potassium chlorate.

6. Bring the solution to a boil and add water until all potassium chlorate has dissolved.

7. Allow the solution to cool slowly. Crystals of potassium chlorate will form. Cool the

solution to 0 deg C.

8. Filter to obtain the raw potassium chlorate. Rinse the crystals in the filter with ice-cold water. The product can be further purified as described below.

Procedure when using calcium hypochlorite

warning: On one occasion an small explosion occurred when I was doing this preparation. I am not sure exactly what caused the explosion. It seems to have been a steam explosion. I was also not sure whether I was using calcium hypochlorite or trichlorohydrocyanuric acid, another common pool chlorinating agent. It seems to be very uncommon that explosions happen and they can probably be prevented by vigorous stirring, but I thought everyone attempting this method should know so proper precautions can be taken. The procedure below has been optimized to reduce the chances of an explosion happening.

1. Place 250 ml of water in a heat resistant glass or stainless steel container, large enough to hold twice that volume.

2. Bring the water to a boil.

3. To the boiling water, add 125 gram of calcium hypochlorite in 10 gram portions. The calcium hypochlorite usually comes in tablets, which need to be crushed first. Stir vigorously during this step, occasionally scraping over the bottom to prevent the formation of a cake of calcium chloride. The solution will foam a lot. If too much foam is developed, do not add any more calcium hypochlorite and boil until the foam subsides. Then continue adding calcium hypochlorite.

4. When all calcium hypochlorite has been added, continue boiling until no more foaming is observed. Stir continuously.

5. Allow the solution to cool down, and filter to remove the precipitated calcium chloride.

6. In a separate container, dissolve 68 grams of potassium chloride in the smallest volume of water possible (approximately 195 ml). This can be done by dissolving the potassium chloride in about 200 ml of water, and allowing it to cool. If crystals form, add some more water, boil again to dissolve the potassium chloride, and allow to cool again. If crystals form, repeat. If not, the solution is ready to use.

7. Mix this solution with the boiled calcium hypochlorite solution. A white precipitate of potassium chlorate should form.

8. Bring the solution to a boil and add water until all potassium chlorate has dissolved.

9. Allow the solution to cool slowly. Crystals of potassium chlorate will form. Cool to 0 deg C.

10. Filter to obtain the raw potassium chlorate. Rinse the crystals in the filter with ice-cold water. The product can be further purified as described below.

3.3 Purifying the product

The product can be purified by recrystallization, just like the product of the electrolytic procedure. For convenience, the same procedure is given again here:

1. Place the crude product in a pan and add 100 ml of water for every 20 g of crude product. Bring this to a boil.

2. Add 20 ml amounts of water to the boiling solution until all the potassium chlorate has dissolved.

3. Check the pH of the boiling solution. It should be neutral or slightly alkaline. If it is acidic, add potassium hydroxide solution until it is slightly alkaline (pH 7..8) again. If this is not done, traces of acid may be included in the product making it very dangerous to use in pyrotechnic compositions.

4. Allow the solution to cool to room temperature. Potassium chlorate will crystallize.

5. Filter and rinse the crystals well with ice cold water. The filtrate may be discarded or concentrated by evaporation and the residue added to the electrolyte for a next batch.

6. The crystals may be dried in an oven at 100 deg C.

Chapter 4: Literature

The amount of literature available is overwhelming. A short list of interesting reading material follows.

1. F Hine, "Electrode processes and electrochemical engineering", Plenum Press, New York (1985)

2. F. Foerster and E. Muller, Z. Elektrochem, **8**, 8, 515, 633, 923 (1902); **9** 171 (1903); **10**, 781 (1904).
Chlorates ; Electrolytic Formation of . F. Foerster

and E. Muller. Z. Elektrochem., 1905, 11, 502—503

THE authors reply to a recent communication by H. Sirk (see this J., 1905, 544). Sirk's experiments dealt with the influence of platinum as electrode material, when free hydrochloric acid is present; and to the preponderance of the second of the two reactions, given in earlier papers by Foerster and Muller, namely—

ClO' + 2HClO-*-ClO3' + 2H' + 2C1',

or the production of chlorate in the electrolytic cell (see this J., 1902, 1235; 1903, 417). The authors here assert that Sirk is in error, in considering that his experi

mental proof that the presence of platinum will accelerate the speed of the reaction represented by the equation:—

C103' + 2H" + 2Cl'-»-C10' + 2HC10,

applies to the reverse reaction, and they re-assert the : correctness of their originally expressed views as to the changes occurring in the electrolytic chlorate cell. These views are based upon the results of direct experiments, and prove that the formation of chlorate is primarily doe to the reaction :—

6C10' + 3HjO + 6©-»-2C10j,' + 4C1' + 6H' + 30,

and is only secondarily due to the reaction investigated by Sirk.^J. B. C. K. "

Nitrites ; Electrolytic Production of , from Nitrtta,

especially with Silver Cathodes. E. Muller and F. Spitzer. Z. Elektrochem., 1905, 11. 509—515.

CONTINUING their former work (this J., 1905, 445), the authors have investigated the cathode potential during the electrolysis of alkaline solutions of sodium nitrate, sodium nitrite, and mixtures of the two, with cathodes of spongy copper, silver and gold. The method of experiment was to record the cathode potential after successive intervals of time, using, in the first place, a platinum cathode, then coating the platinum cathode with a smooth deposit of the metal in question, and adding successive quantities of the metallic nitrate dissolved in a liquid of the same composition as the electrolyte, and continuing the observations after each such addition. The results with silver are in general similar to those formerly obtained with copper, that is to say, with the smooth cathode the potential required for the reduction of the nitrate, at first below that needed

i for the reduction of the nitrite, soon rises above it and remains there, whilst with the spongy cathode the potential needed to reduce the nitrate is uniformly below that needed to reduce the nitrite. The difference in the latter case, however, is very much greater with silver than with copper, so that the reduction of the nitrate to nitrite can be carried very much nearer to completion before any reduction of nitrite to ammonia occurs. In an actual experiment with a cathode of spongy silver between iron anodes, nearly 4 grms. of nitrite were formed in three hours in a solution originally containing 23-1 grms of nitrate. and 27-5 grms. of nitrite, 96 per cent, of the current being thus utilised; and when the original solution contained only 7-9 grms. of nitrate and 45 grms. of nitrite, a yield of nitrite corresponding to 48-5 per cent, of the current was still obtained. Elevation of temperature *is* not favourable to the yield of nitrite. A previously prepared spongy electrode did not work as well as one formed during the process in the manner above described; the

I removal of this disability in the previously formed cathode is of importance, for there are great difficulties in the way of adding silver solution and forming the cathode during electrolysis, if the process is to bo worked industrially. A fairly complete conversion of the nitrate present into nitrite is necessary, as otherwise the isolation of the nitrite by crystallisation is impracticable. Gold cathode?, whether smooth or spongy, are not suitable for nitrite production, as with them the reduction of the nitrite to

, ammonia occurs at the same potential as and concurrently with the production of the nitrite.—J. T. D.